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Waste Oil Heaters: Organic, Inorganic, and
Bioassay Analyses of Combustion Samples

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WASTE OIL HEATERS:
ORGANIC, INORGANIC, AND BIOASSAY
ANALYSES OF COMBUSTION SAMPLES

by

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16. ABSTRACT The paper describes tests on two typical designs of waste-oil space heaters, firing two different types of waste crankcase oils. Study results can be summarized according to the four substances investigated: particulates, polynuclear aromatic hydrocarbons (PAHs), organolead, and fuel samples. Analysis of samples from the air atomizing heater (AAH) confirmed previously identified elevated metal content of waste oil emissions. Bromine levels were exceptionally high. The ferrous ion (Fe(II)) content in particulate samples from the AAH was very low. Several PAHs were at elevated levels in gaseous emissions from both space heaters: the vaporizing pot heater (VPH) emissions had the higher PAH content. No organolead was detected in emissions from the AAH (organolead analyses were not performed on the VPH emissions). Mutagenicity assays of the particulate and the XAD samples from both heaters were mutagenic and contained direct-acting mutagens: emissions from the VPH were the more mutagenic. Comparison of the two types of fuels showed that emissions from the automobile waste crankcase oil were consistently more mutagenic than those from the truck waste crankcase oil.			
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Combustion		Waste Oil	21B
Space Heaters		Automotive Oil	13A
Bioassay		Air Atomizing Burners	06A
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I. Introduction

In recent years federal, state, and local agencies have focused attention on emissions from the combustion of waste crankcase oil. Due to the sharp rise in the price of natural gas, fuel oil, and electricity, businesses that have an abundant supply of waste crankcase oil are using it for space heating in large areas, such as garages. Unfortunately, most waste crankcase oils contain large amounts of trace metals.

In order to obtain emissions data which could be used by concerned government agencies and industry, the U.S. Environmental Protection Agency's Office of Research and Development has sponsored tests on two typical designs of waste oil space heaters firing two different types of waste crankcase oils. The tests were performed by EPA's Industrial Environmental Research Laboratory in Research Triangle Park, NC.

II. Test Equipment and Fuels

Two types of waste oil heaters were tested while firing filtered, but otherwise untreated, waste crankcase oils. One was a Kroll Model W400L, waste oil heater rated at 35.2 kW (120,000 Btu/hr heat input). It uses a vaporizing pot burner in which only the heated vaporized fuel is combusted. With this type of burner the residue of unburned material, which accumulates in the bottom of the fuel pot, must be physically removed. This residue was also analyzed for organic and inorganic content. The second unit tested in this program was a Dravo Hastings Thermoflo Model 20-WO, waste oil heater rated at 73.3 kW (250,000 Btu/hr heat input), and it utilizes an air atomizing burner. With this type of burner, most of the fuel is burned and discharged as stack effluent.

Two different types of waste crankcase oils were tested during the Phase 1 study. One was an automotive waste crankcase oil that was obtained from a service station. The other was a truck crankcase oil that came from a diesel truck fleet. Since the emissions resulting from combustion of the automotive waste crankcase oil were higher, it was the only waste oil studied during the Phase 2 study.

III. Background

As a result of the Phase 1 tests (1,2), several trace metals were identified which were emitted into the atmosphere in high concentrations. It was found that burner design and fuel composition both have a significant effect on the levels of inorganic elements emitted. As shown in Figure 1, the air atomizing burner allowed high levels of trace elements to be carried by the flue gas into the stack. It also had particulate mass emission levels that were an order of magnitude higher than those of the

vaporizing pot burner. The vaporizing pot burner retained a significant amount of the trace elements in the pot residue. The study also showed that, even though total organic emissions from the two burners are similar, higher levels of polynuclear aromatic hydrocarbons (PAHs) were found in discharges of the vaporizing pot burner.

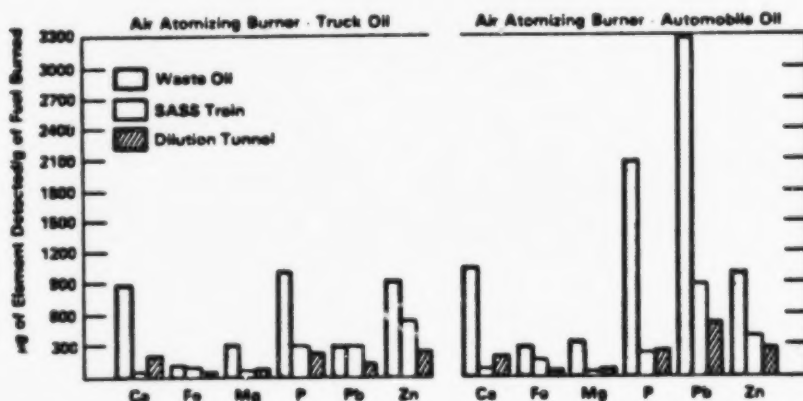


FIGURE 1. COMPARISON OF TOTAL MASS OF ELEMENTS DETERMINED BY ICAP FOR THE AIR ATOMIZING HEATER BURNING AUTOMOTIVE AND TRUCK CRANKCASE OIL.

As a result of the Phase 1 screening studies, it was decided that a Phase 2 follow-on study was needed to provide more information about specific chemical species in waste crankcase oil emissions. PAHs were analyzed in more detail, elemental analyses (including Pb, Fe, Cd, Zn, Cl, and Br) were performed on the air atomization burner discharges, and analyses were conducted to measure possible organolead constituents and to determine the distribution of iron oxidation states (Fe(II) and Fe(III)).

In addition to the chemical analysis, a microbial mutagenicity assay was performed on the samples collected. The *Salmonella typhimurium* mutagenicity test developed by Ames et al. (3) has been widely used to evaluate the mutagenicity and potential carcinogenicity of pure chemicals and complex environmental samples. This assay detects substances that cause frameshift and base-pair substitution mutation in histidine-requiring mutants, that revert to prototrophy as a result of exposure to the mutagen. The Ames assay was used in this study to evaluate the potential carcinogenicity of the combustion products from the truck and automotive waste crankcase oils.

IV. Test Measurements

In addition, data were obtained for an EPA Level 1 assessment. This required the use of a glass Source Assessment Sampling System (SASS) train with subsequent data reduction by Battelle-Columbus Laboratories. The analysis included: spark source mass spectroscopy (SSMS) using an AEI Model MS-702R instrument to screen elemental constituents; inductively coupled argon plasma (ICAP) spectrometry using a Jarrell-Ash Model 975 instrument to analyze elemental species; and atomic absorption spectroscopy (AAS) using a Perkin-Elmer Model 5000 instrument to provide mercury (Hg), arsenic (As), and antimony (Sb) emissions data. Total chromatographable organic (TCO) analyses, gravimetric (GRAV) analyses, infrared (IR) analyses, and low resolution mass spectroscopic (LRMS) analyses were performed to obtain information about organic emissions.

A slipstream of the stack effluent was ducted into a dilution tunnel where a flow of filtered dilution air was allowed to mix with the heater discharge at a ratio of 10:1. The entire dilution tunnel effluent was collected in a Massive Air Volume Sampler (MAVS). The MAVS is a device normally used for ambient air sampling. It contains Teflon-coated metal plates which act as an electrostatic precipitator (ESP). This allows large amounts of particulate to be collected which can be easily removed for chemical and bioassay analysis. The dilution tunnel simulates the dilution and mixing that would occur if the flue gas were discharged directly into the environment. Organic bioassay samples used in this study were collected on a 51 cm x 51 cm (20 in. x 20 in.) Teflon-coated Paliflex filter.

The sampling conditions for the two stack effluent samplers (SASS train and dilution tunnel) are given in Table I for both types of waste oil heaters firing the automotive and truck waste crankcase oil fuels.

A comparison of total organic material collected in the Level 1 study is shown in Figure 2 where both burner types are compared for the two sampling strategies, SASS train and dilution tunnel.

The objective of the Phase 2 study was to perform detailed investigations on waste oil emission species identified or suspected from Level 1 data generated in the earlier program. The experimental portion of this study consisted of five parts:

- (1) Analysis of PAHs in gaseous emissions from a vaporizing pot heater (Kroll) and an air atomization combustion system (Dravo)
- (2) X-ray fluorescence analysis of inorganic species, including Br, I, Fe, Cd, Pb, and Zn, in particulate discharges from the air atomization heater.
- (3) Analysis of the Fe(II)/Fe(III) ratio in the air atomization gaseous effluent.

TABLE 1. SAMPLING DATA

Sampling Condition	Vaporizing Burner		Air Atomizing Burner	
	Automotive	Truck	Automotive	Truck
Average stack temperature, °C (°F)	414 (777)	416 (781)	339 (642)	332 (630)
Alnor reading, m/min (ft/min) at stack conditions	129 (424)	126 (412)	84 (275)	88 (288)
Stack diameter, cm (in.)	15.2 (5.98)	15.2 (5.98)	22.9 (9.02)	22.9 (9.02)
Total volume sampled, SASS, m ³ (ft ³)	30 (1060)	32 (1100)	15 (530)	29 (1020)
Total volume sampled, dilution tunnel, m ³ (ft ³)	126 (4450)	80 (2800)	77 (2700)	117 (4130)
Volumetric flow rate (Q) at STP (20°C, 1 atm.), m ³ /sec (ft ³ /sec)	0.015 (0.53)	0.014 (0.49)	0.024 (0.85)	0.024 (0.85)
Fuel feed rate, l/hr (gal/hr)	2.5 (0.66)	2.5 (0.65)	5.91 (1.56)	5.31 (1.56)

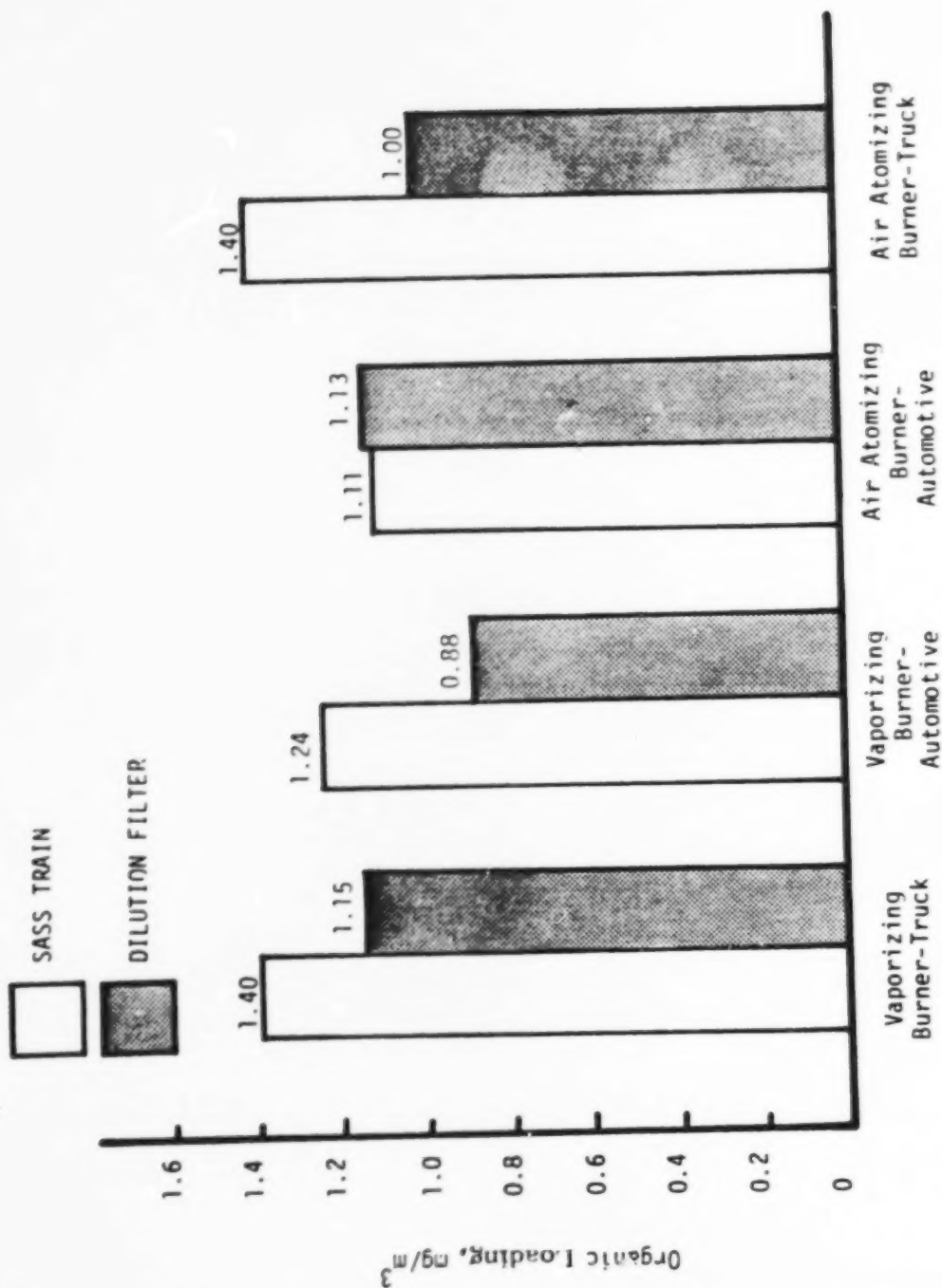


FIGURE 2. COMPARISON OF TOTAL ORGANICS FOR EACH TEST RUN SAMPLED BY SASS TRAIN AND DILUTION TUNNEL.

- (4) Analysis of air atomization gaseous discharges for organolead composition.
- (5) Detailed bioassay, analyses of the SASS and dilution tunnel samples collected in the Level 1 study.

To complete the speciation measurements outlined above, two special sampling systems were used to collect suitable samples. A Modified Method 5 train (MM5), shown in Figure 3, was used to collect the samples for PAH and metals analysis. MM5 samples were collected for both air atomization and vaporizing pot burners in order to measure PAH emission levels. Metals speciation tests were performed only in the air atomization tests since Level 1 data revealed elevated metal discharges from air atomization burning.

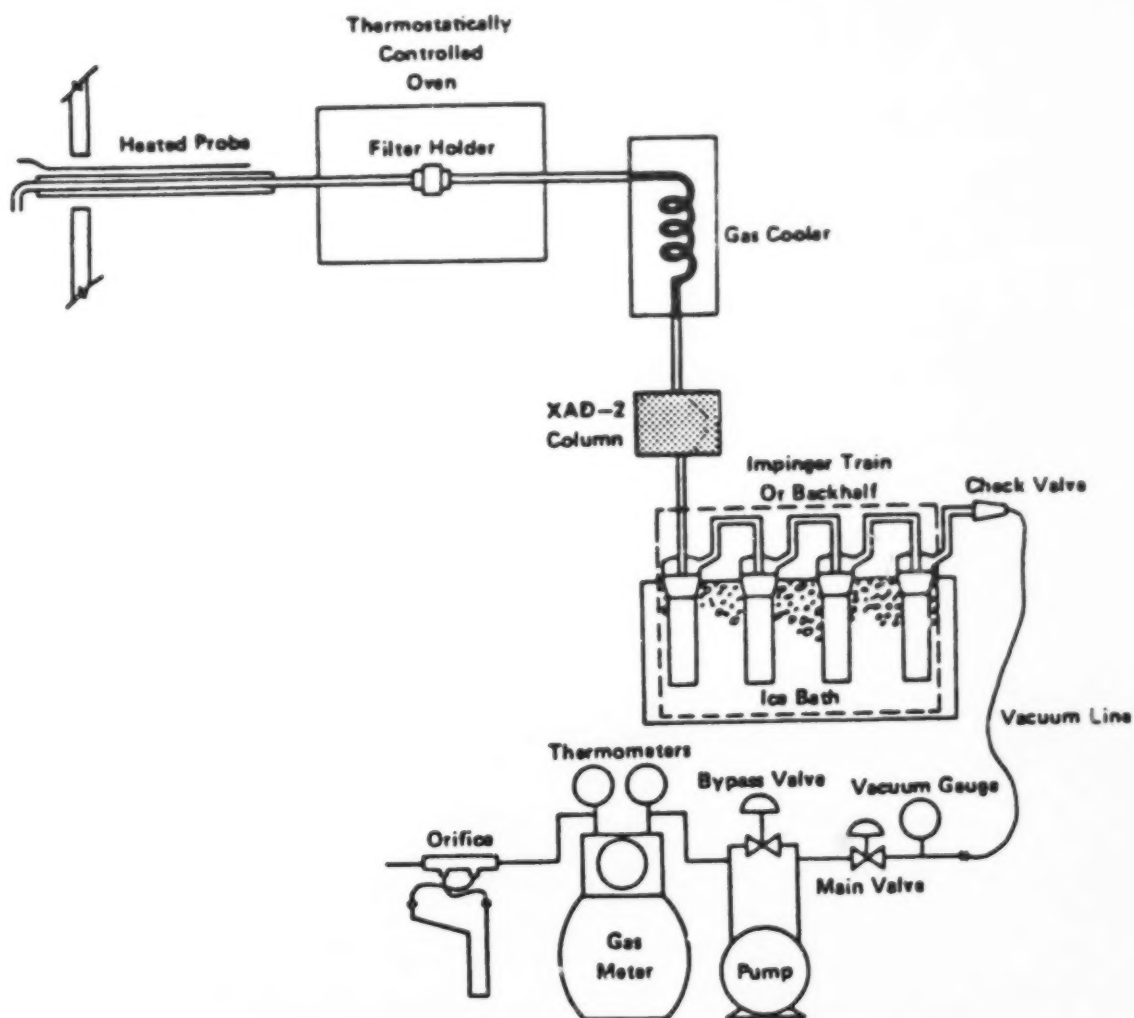


FIGURE 3. THE MODIFIED METHOD 5 (MM5) TRAIN.

The sampling conditions used for the vaporizing pot MM5 samples are given in Table II, while the air atomization MM5 sampling conditions are given in Table III.

The organolead samples required development of a cryogenic sampling system designed to condense the large amount of water found in a combustion source. Several designs tested would trap a plug of ice, thus closing off the flow stream. The cryogenic sampler used in this study is shown schematically in Figure 4 and is fully discussed in the EPA report describing this study (4).

V. Analytical Methods

Particulate Emissions

The substances of interest in the analysis of the MM5 particulate filter samples were those species which had been detected in the Phase I study at relatively high levels in waste oil combustion emissions: iodine (I), cadmium (Cd), iron (Fe), zinc (Zn), lead (Pb), chlorine (Cl), and bromine (Br). Since iron was identified as one of the predominant metallic elements in waste oil combustion emissions, an attempt was made to identify the relative amounts of the Fe species in the particulate emission samples. Consequently, two analyses were conducted on the MM5 particulate samples: X-ray fluorescence analysis of the seven elemental species of interest and a ferrous ion (Fe(II)) determination to allow a calculation of the $\text{Fe(II)}/\text{Fe(III)}$ ratio in the emissions.

X-Ray Fluorescence Analyses--

X-ray fluorescence analyses were performed on three MM5 filter catches from the air atomization heater tests. Two of the filter samples, designated No. 3 and No. 5, were partial runs with weights of 0.6527 g and 0.5932 g, while No. 6 represented a complete test run and had a net weight of 0.8719 g. The analyses were conducted with a Kevex Energy Dispersive X-ray Analyzer. This instrument possesses the capability of a computer-controlled fundamental parameter program to obtain quantitative results.

Ferrous Ion Analysis--

The ferrous ion (Fe(II)) content of the three air atomization MM5 filter samples was determined using a bathophenanthroline photometric method. The principle of the method is based on the formation of ferrous bathophenanthroline complex in a solution buffered at pH 5 with subsequent extraction in chloroform. The absorbance of the complex at 533 nm was used to estimate the ferrous ion content from a previously prepared calibration curve. The calibration curve was constructed using ferrous ammonium sulfate as a standard. The filter samples were prepared by weighing the filter and

TABLE II. TEST CONDITIONS FOR VAPORIZING
POT COMBUSTION EXPERIMENTS

	Run 1		Run 2	
Barometric pressure, MPa (in. Hg)	0.102	(30.2)	0.102	(30.1)
Stack temperature, °C (°F)	411	(711)	419	(786)
Stack velocity, m/sec (ft/sec)	3.7	(12.2)	3.7	(12.2)
Meter temperature, °C (°F)	38	(101)	40	(104)
Isokinetic variation, %	112.7		109.7	
Corrected dry volume, scm (scf)	3.6	(126)	4.0	(143)
Moisture volume, scm (scf)	0.29	(10.4)	0.31	(11.1)
Flue gas composition				
H ₂ O, %	7.7		7.2	
CO ₂ , %	7.3		7.0	
O ₂ , %	11.7		11.8	
CO, ppm (v/v)	10		10	
Calculated molecular weight	28.87		28.87	
Auto crankcase oil used, l (gal)	15	(4)	14	(3.7)
Test time, minutes	280		330	
Rate, l/hr (gal/hr)	3.2	(0.85)	2.5	(0.66)
Pot residue, g	290		310	
Residue deposition rate				
g/cc	0.0193		0.0222	
g/min	1.03		0.94	
Average ΔP @ orifice plate, Pa (in. H ₂ O)	158	(0.635)	175	(0.703)

TABLE III. TEST CONDITIONS FOR AIR ATOMIZATION
COMBUSTION EXPERIMENTS

	Run 1		Run 2	
Barometric pressure, MPa (in. Hg)	0.102	(30.2)	0.102	(30.1)
Stack temperature, °C (°F)	266	(511)	266	(511)
Velocity, m/sec (ft/sec)	1.4	(4.6)	1.4	(4.6)
Meter temperature, °C (°F)	40	(104)	40	(104)
Isokinetic variation, %	657		361	
Corrected dry volume, scm (scf)	4.3	(151)	3.3	(117)
Moisture volume, scm (scf)	0.40	(14)	0.34	(12)
Flue gas composition				
H ₂ O, %	8.3		9.3	
CO ₂ , %	10-11		10-11	
O ₂ , %	6.8		6.8	
CO, ppm (v/v)	50		50	
Calculated molecular weight	28.36		28.24	
Auto crankcase oil used, l (gal)	22	(5.81)	31	(3.21)
Test time, minutes	220		311	
Rate, l/hr (gal/hr)	7.3	(1.6)	7.3	(1.6)
Average ΔP @ orifice plate, Pa (in. H ₂ O)	520	(2.1)	92	(0.37)

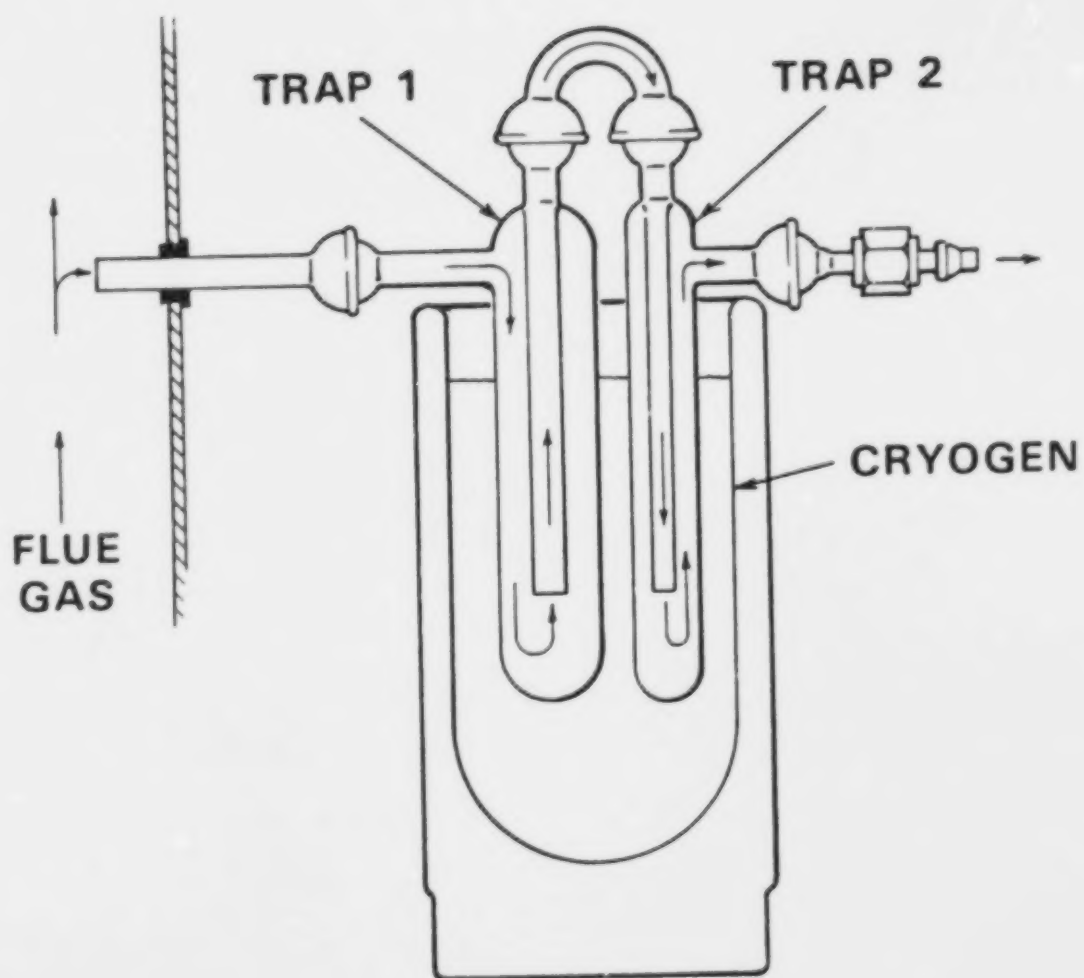


FIGURE 4. CRYOGENIC SAMPLING TRAIN FOR COLLECTING VOLATILE ORGANOLEAD EMISSIONS.

digesting the sample in 50 ml of 5% HCl under a CO₂ atmosphere. The cooled solution was diluted to 100 ml, from which a 20 ml aliquot was treated with the bathophenanthroline reagent.

PAH Emissions

The four MM5 train samples collected in the combustion tests were analyzed for PAH by high resolution gas chromatography mass spectrometry (HRGC/MS). To prepare for this analysis, the XAD-2 resin sample was extracted with methylene chloride, along with the particulate-laden filter, in a Soxhlet extractor. The filter was re-extracted separately with benzene to remove PAH compounds not extracted by methylene chloride. The resin-filter extract was combined with the extracts of the aqueous impinger. This combined sample, which contained most of the organic burden, was analyzed by gas chromatography and gravimetry to determine condensible organics. The combined organics sample and the benzene filter extract were then combined and reduced to about 1 ml with a Kuderna-Danish concentrator, and to a final volume of 0.5 ml by directing a gentle stream of nitrogen across the top of the sample. An internal standard was spiked into the sample at this point before analyses by HRGC/MS.

Organolead Compounds

As with the sampling system for organolead compounds, an analytical method had to be developed for the determination of these compounds. Lead alkyls are a common fuel additive, used as an antiknocking ingredient in gasoline. The principal species used commercially are the methyl and ethyl substituents, predominantly tetramethyl (TML), trimethylethyl (TMEL), dimethyldiethyl (DMDEL), methyltriethyl (MTEL), and tetraethyl (TEL) lead.

The method most commonly used to measure alkyl lead compounds is gas chromatography (GC) coupled to an atomic absorption spectrometer (AAS) (5). The AAS acts as a sensitive detector for lead. Radziuk *et al.* used cryogenic sampling and GC/AAS to measure ambient alkyl lead with a graphite furnace technique to demonstrate instrument sensitivity of 40 pg Pb, which corresponded to about 0.5 ng/m³ in a 70 liter air sample (6). After experimenting with the GC/AAS interfaces proposed in the literature, a modification was used in this study which improved instrument sensitivity for direct flame atomization. This modified interface consisted of a 0.3 cm (1/8 in.) (O.D.), stainless steel GC tube mounted directly into the base of the AAS burner and attached to the GC column. The effluent from the GC column is passed through this tube and the entire effluent uniformly aspirated across the flame front.

The GC/AAS system used was a Varian Model 1400 GC interfaced to a Perkin Elmer Model 5000 AAS. The GC was equipped with a 0.9 m (3 ft) x 0.64 cm (0.25 in.) (O.D.) stainless steel column packed with 10% (W/W) Carbowax 20M on 100/120 mesh Porasil C. The column was held isothermal at 130°C and helium (120 ml/min) was the carrier gas. The reference standard

used for calibration was provided by the Ethyl Corporation (MLA-500(T313)) and contained 1.53 mg Pb per ml of solution in isooctane. The concentrations, retention times, and estimated detection limits for the individual tetraalkyl lead species in the reference mixture are given in Table IV.

TABLE IV. ALKYL LEAD REFERENCE MIXTURE -
MLA-500(T313)

Compound	Concentration, $\mu\text{g/ml}$	Retention Time, min	Detection Limit, ng
TML	114	0.61	11
TMEL	336	0.78	22
DMDEL	548	1.17	30
MTEL	408	1.78	47
TEL	123	3.00	81

Chromatograms showing the separation and rapid elution (<4 min) capabilities of the GC/AAS system are shown in Figure 5. The upper chromatogram shows a 50 μl injection representing 5.7-27.4 μg of the alkyl lead compounds. The lower chromatogram shows a 5 μl injection representing 0.6-2.7 μg of each compound. At high sample loading on the GC column, as shown in the upper chromatogram, TML and TMEL show overlap and loss of resolution. Resolution is restored by reducing the amount of sample analyzed.

VI. Mutagenicity Bioassay Method

The fuel and organic extracts of the SASS samples (XAD only), and the filter samples from the dilution tunnel, for combustion of automotive and truck waste crankcase oils, using both atomizing and vaporizing burners were bioassayed for mutagenicity (7). The standard Salmonella typhimurium plate incorporating assay with minor modifications (3,8) was performed. The filter and resin samples were Soxhlet extracted with dichloromethane for 24 hours. The extract was then solvent-exchanged into dimethyl sulfoxide (DMSO). The organic extracts and the DMSO slurry of the waste oils were

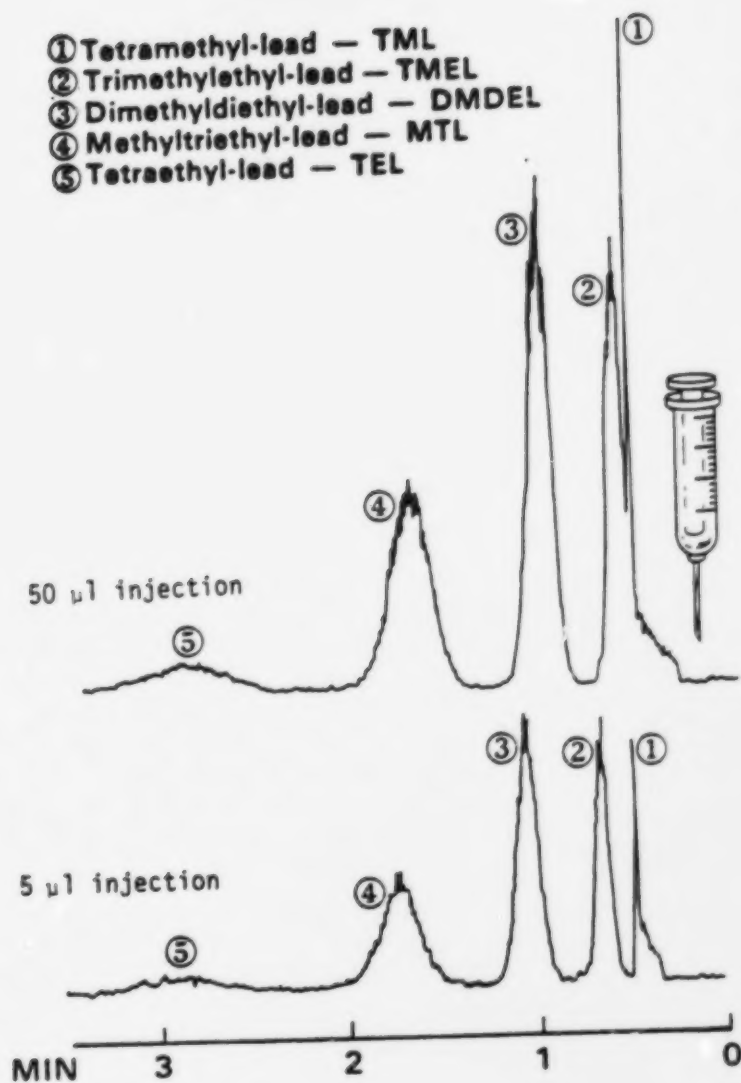


FIGURE 5. CHROMATOGRAMS OF TETRAALKYL LEAD COMPOUNDS IN THE GC/AAS SYSTEM.

tested, with and without S9 metabolic activation (the Aroclor-induced rat liver 9000 x g homogenate) in *Salmonella typhimurium* tester strain TA98. The data were analyzed using the nonlinear model to determine the slope of the dose response curve (9).

VII. Results

Organolead Compounds

Analysis of cryogenic samples from the air atomization burner tests indicated that no organolead compounds were present in the emissions. Since alkyl lead species are most likely not formed in the combustion conditions found in burning waste crankcase oil in the air atomizer combustor, the presence of these compounds would be an indication of unburned organolead additives in the waste oil fuel. To determine if organolead compounds were present in the crankcase oil used to fuel the air atomization burner, the waste oil was analyzed directly with the GC/AAS system and produced no measurable alkyl lead signal. The fuel oil then was spiked with a known addition of the Ethyl Reference Standard and analyzed by direct injection onto the GC/AAS analytical system. The chromatogram from that analysis is given in Figure 6. This chromatogram shows measurable peaks (except for TEL) near the detection limit.

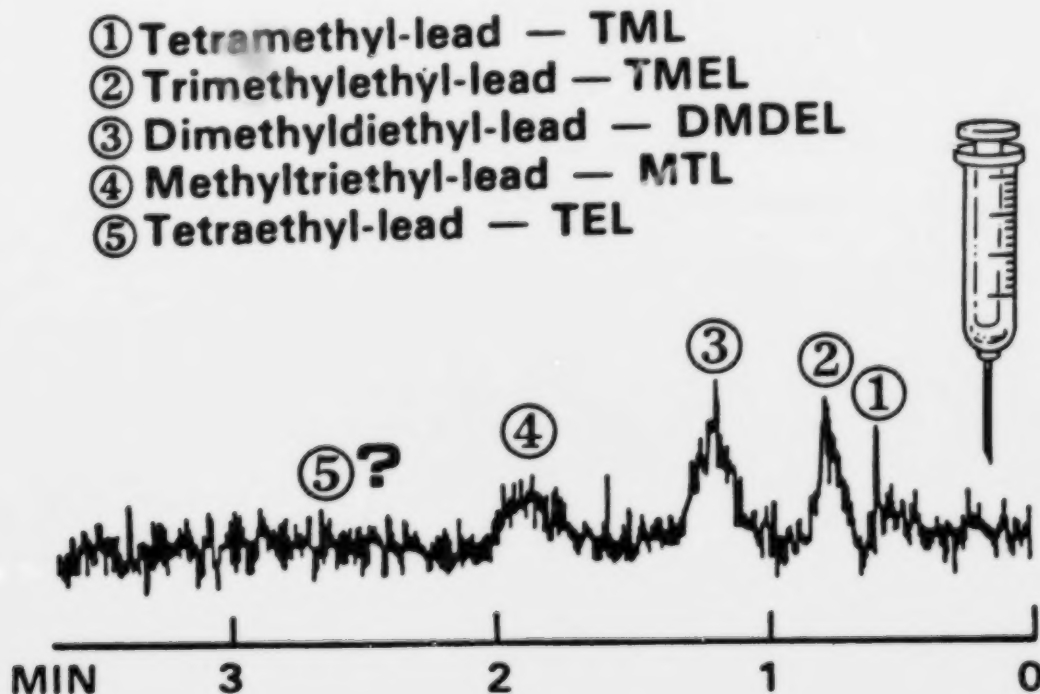


FIGURE 6. GC/AAS CHROMATOGRAM OF THE SPIKED WASTE OIL FUEL BY DIRECT INJECTION.

If organolead compounds were present in the fuel, they would be at extremely low levels. From the GC/AAS method detection limits cited earlier, this method should measure approximately 20 $\mu\text{g TML}/\text{m}^3$ in flue gas emissions and about 25 mg TML/l in the waste oil fuel. From the previous Level 1 analysis of air atomization burners using the same automobile crankcase oil for fuel (1), a flue gas lead concentration of 140 mg/m³ and a waste oil concentration of about 3 g/l were found. These concentrations, total lead in waste oil fuel and flue gas discharge, are far above the demonstrated method detection limits for the GC/AAS method. If lead were appreciably present in an organometallic form in these samples, it should be measurable. These data indicate that organolead compounds could be only a minor constituent of the air atomizer discharges measured in this study. No organolead analyses were made on vaporizing pot burner emissions.

Organolead compounds have been estimated to be a small percentage (0.1-14%) of total ambient lead (10-12). Radziuk *et al.* (6) found that tail-pipe emissions of alkyl lead are a minor fraction of ambient organolead levels. Volatile lead compounds in the ambient air arose from vaporization of gasoline and volatile lead losses from liquid fuels, not from combustion in internal combustion engines. The same effect would be expected from waste oil combustion. Waste crankcase oil combustion should be of minor concern for producing organolead emissions in the ambient air.

Ferrous Ion Analyses

The results of the analysis of the ferrous ion (Fe(II)) content in the MM5 particulate samples from the air atomization heater are given in Table V.

TABLE V. FERROUS ION CONTENT OF FILTER SAMPLES

Sample Number	Total Filter Weight, g	Fe(II) Content		Total Fe Content, ^a μg
		Total μg	$\mu\text{g/g}$ (ppm)	
3	0.6527	62	95	11,900
5	0.5932	52	88	9,100
6	0.8719	74	85	19,200

a As determined by X-ray fluorescence

These data indicate that Fe(II) is present at relatively insignificant levels in emissions from the air atomization heater fueled with automotive waste oil. Comparison of Fe(II) data with the X-ray fluorescence results for total Fe content shows that Fe(II) constitutes only a minor portion of the Fe content in these emissions. Since iron is expected to be converted primarily to ionic forms in combustion processes, an assumption can be made that only a relatively small amount of iron will be in the elemental state. Consequently, the amount of Fe(III) in the sample can be estimated by subtracting the Fe(II) content from the total Fe content. The resulting values for Fe(III) are relatively large, and the Fe(II)/Fe(III) ratios would, therefore, be small. The predominant form of Fe in the waste oil combustion emissions is, therefore, Fe(III).

PAH Emissions

PAH emissions are of concern since several members of this class of organic compounds are considered to be mammalian carcinogens. The results of PAH analyses are presented in Table VI. In general, the vaporizing pot samples showed higher concentrations of individual PAH species than the air atomization samples. Since Runs 1 and 2 were intended to be duplicates, and were very similar in test conditions and sampling parameters, the observed test-to-test differences reflect the variability of these data.

The data in Table VI are corrected for a system blank analysis, but are not corrected for method recoveries. Method losses were estimated by the technique of labeled isotope addition. In this method, a known amount of an atomic isotope of the compounds analyzed is spiked into the MM5 train after sampling. The recovery standard in this analysis was benzo(a)pyrene (BaP-d₁₂). These spikes were administered by liquid injection of 40 µg BaP-d₁₂ in benzene solution onto the XAD-2 resin. Quantitative (approximately 100%) recoveries were found for the BaP-d₁₂ spikes.

The complexity of the waste oil combustion discharges is illustrated by the total ion chromatogram of the air atomization sample shown in Figure 7. This chromatogram represents a simpler peak pattern where extracted ion chromatography is used to improve analytical sensitivity.

Salmonella Mutagenicity Assay

The uncombusted automotive oil showed low mutagenicity (0.09 revertants/µg with exogenous activation and 0.03 revertants/µg without activation in strain TA98) and the truck oil showed no mutagenic activity. The emissions from both burner types using automotive and truck oils were mutagenic and contained direct-acting mutagens. In comparison with other combustion emissions and based on revertants/µg organics, the mutagenicity of the organics extracted from the particles from waste oil combustion was comparable to or more mutagenic than the organics of the particles emitted from a residential wood stove, but

TABLE VI. RESULTS OF PAH ANALYSES

Compound	Amount Detected, $\mu\text{g}/\text{m}^3$ dry			
	VP-Run 1 ^a	VP-Run 2 ^a	AA-Run 1 ^a	AA-Run 2 ^a
Naphthalene	12	6	5	4
Acenaphthene	--	--	0.3	0.2
Acenaphthylene	2	--	--	--
Fluorene	6	0.6	0.8	0.7
Phenanthrene	70 ^b	5	6	4
Anthracene	--	2	0.2	0.2
Fluoranthene	--	--	0.4	0.5
Pyrene	3	2	0.5	0.5
Benzo(a)anthracene	--	4	0.2	0.4
Chrysene	--	--	0.2	0.4
Benzo(a)fluoranthene	--	6	--	--
Benzo(e)pyrene	5	6	--	0.05
Benzo(a)pyrene	6	8	--	1
Perylene	--	6	--	0.6
Indeno(1,2,3-cd)pyrene	--	--	--	0.8
Benzo(ghi)perylene	--	--	0.1	0.6
Anthanthrene	--	--	0.1	1.1
Coronene	--	--	--	0.1

^a VP = Vaporizing Pot Sample; AA = Air Atomization Heater Sample

^b This apparent high result was verified by fragment ion patterns and appears to be an outlier.

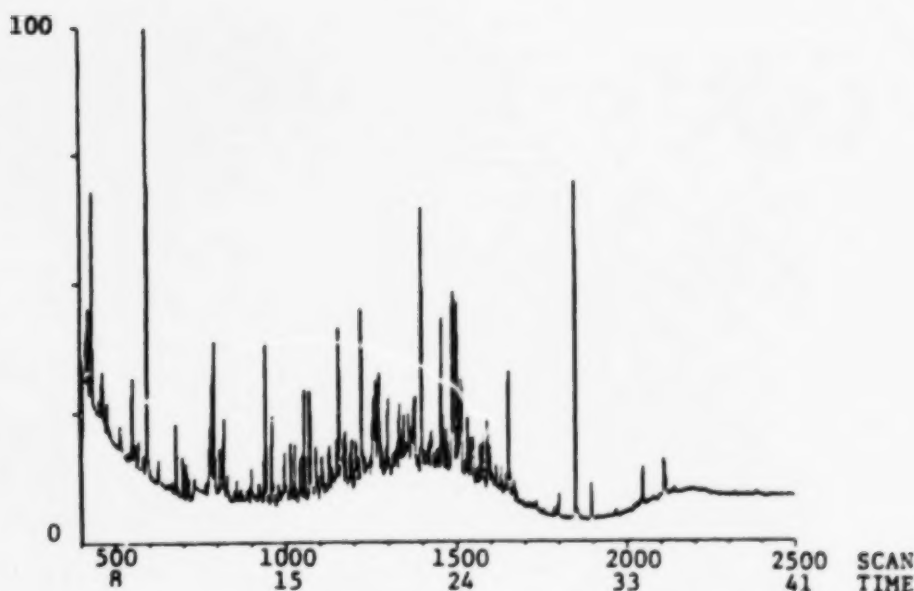


FIGURE 7. HRGC/MS TOTAL ION CHROMATOGRAM OF A VAPORIZING POT SAMPLE.

less mutagenic than from many diesel or gasoline engine exhausts or a residential oil heater (13). In order to calculate the mutagenic emission rate, the mutagenicity of the organic extracts (revertants/ μg) was multiplied by the organic emission rate ($\mu\text{g}/\text{m}^3$). Figure 8 shows the mutagenic emission rate of the SASS XAD and the dilution tunnel samples from waste oil combustion in *Salmonella typhimurium* TA98 with and without metabolic activation. Comparison of the two types of fuels used shows that the emissions from automotive oil combustion were consistently more mutagenic than the emissions from truck oil combustion. Within the same type of fuel, either automotive or truck oil, the emissions from the vaporizing burner were more mutagenic than the emissions from the atomizing burner.

VIII. Discussion

The results from this study can be summarized according to the four substances investigated: particulate emissions, PAH emissions, organolead compounds, and fuel samples.

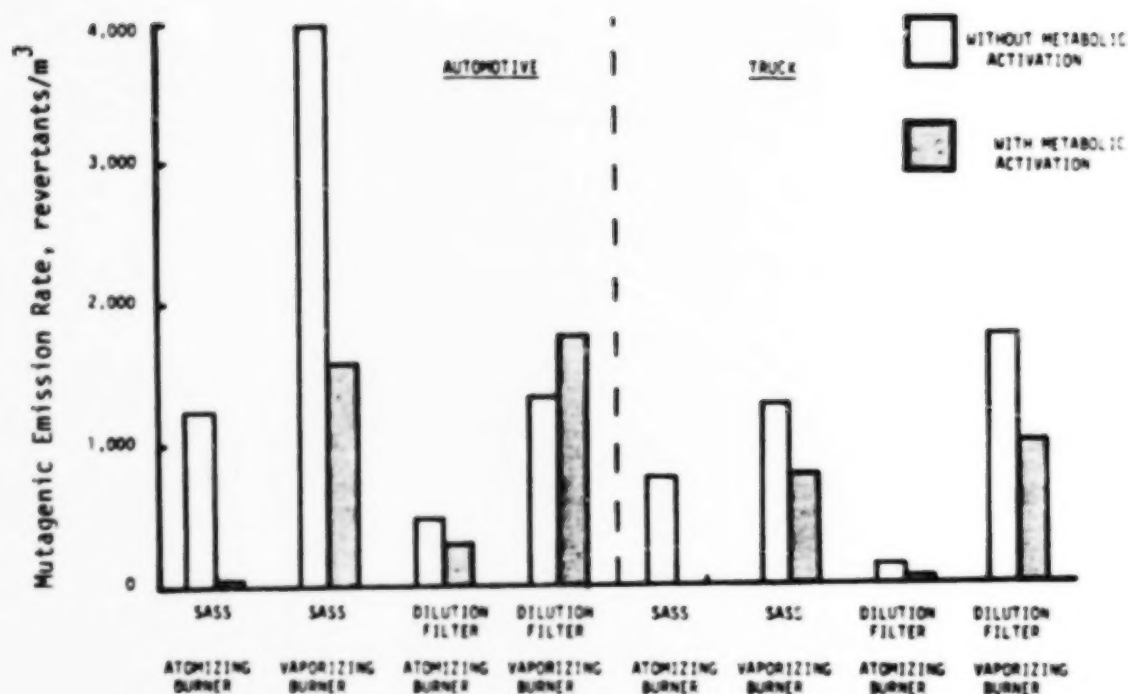


FIGURE 8. MUTAGENICITY OF EMISSIONS FROM WASTE CRANKCASE OIL COMBUSTION IN *SALMONELLA TYPHIMURIUM* TA98 WITH AND WITHOUT S9 ACTIVATION.

Particulate Emissions

Analysis of elemental species in emission samples from the air atomization heater confirmed the elevated metal content of waste oil emissions previously identified in the Phase I study. Bromine levels were exceptionally high, indicating that bromine from gasoline anti-knocking additives exists as a major constituent of waste crankcase oil and represents a major air emissions constituent from this source. Fe(II) content in particulate emissions from the air atomization heater was very low. Based on the results of the Fe(II) analyses and on the assumption that iron exists primarily in ionic forms in combustion emissions, Fe(III) was determined to be the major Fe species in emissions from the air atomization heater fired with waste oil.

PAH Emissions

Several PAH compounds were found at elevated levels in gaseous emissions from both residential heaters tested. Vaporizing pot emissions had a higher PAH content than the air atomization heater and, based on literature estimates, also higher than residential heaters fired with distillate fuel oil.

Many liquid combustion fuels (gasoline, diesel fuel, No. 2 fuel oil) have elevated PAH levels. Fuel and emission PAH levels for several stationary and mobile combustion sources are compared in Table VII. This comparison is made by using a single compound as an indicator molecule. The compound selected is benzo(a)pyrene, which is probably the most extensively studied PAH compound due to the early identification of this substance as an animal carcinogen. From the data in Table VII, it is apparent that many liquid fuels have high inherent BaP levels if discharges and fuels are compared on a weight-of-fuel-consumed basis. The waste oil heaters discharge higher BaP levels than all of the sources compared in Table VII, including equivalent space heaters using No. 2 fuel oil. The removal of lead antiknocking additives from automotive fuel poses a dilemma to the environmentalist. Lead is commonly replaced with aromatic constituents which results in fuels with aromatic content as high as 50-70%, such as found in Europe (18). While ambient lead levels are diminishing, and concurrently the hazard of gasoline antiknocking additives entering residential combustion sources via waste crankcase oil is also alleviated, the high aromatic content of unleaded fuel may actually increase PAH levels. PAH levels are also rising with the increased use of diesel-powered vehicles in the United States. This trend could affect ambient air quality. One researcher estimates that mobile sources currently contribute about 20% of the U.S. ambient burden of PAHs (16).

Organolead Compounds

No organolead compounds were detected in emissions from the air atomization heater. The sampling and analysis methods developed in this study for determination of volatile organolead emissions should be useful in determinations of other organometallic species in combustion emissions.

Health Effects

In this study, the waste automotive crankcase oil showed low mutagenicity in the *Salmonella* mutagenesis assay. Grimmer et al. (19) reported that automotive waste crankcase oil produced dose-related skin tumors in mice. The PAH fraction containing more than three rings accounts for about 70% of the total carcinogenicity even though the PAH fraction constitutes only up to 1.14% of the total oil sample by weight. Waste

TABLE VII. COMPARISON OF BENZO(a)PYRENE CONCENTRATIONS
REPORTED IN RAW FUELS AND COMBUSTION EMISSIONS

	Fuel ^a ppm (W/W)	Combustion Emissions ppb (W/W)
<u>Mobile Sources</u>		
Car - gasoline (catalyst)	0.9 - 9	0.4 ^b
Car - gasoline (no catalyst)	0.9 - 9	5.0 ^b
Diesel engine	1	10.0 ^b
<u>Stationary Sources</u>		
Coal-fired power plants	--	0.5 - 3.5 ^c
No. 2 oil-fired power plants	0.01 - 0.05	0.3 - 2.0 ^c
No. 2 oil-fired residential heaters	0.01 - 0.05	0.1 ^b
Waste oil-fired residential heaters		
Vaporizing pot heater - automotive	4 - 17 ^d	550
Air atomizing heater - automotive	4 - 17 ^d	13

- a Reference 14 - Guerin (1978)
 b Reference 15 - Grimmer (1979)
 c Reference 16 - Ramdahl, et al. (1983)
 d Reference 17 - Becker and Comeford (1980)

crankcase oil has been proposed as a listed hazardous waste under the Resource Conservation and Recovery Act (20). The crankcase oil may pose an occupational hazard to mechanics or other workers exposed to crankcase oil on their hands (21).

In this study, the waste oil combustion products proved to be mutagenic using the Salmonella mutagenicity assay. Both burner types emitted direct acting mutagens. The emissions from automotive oil combustion were consistently more mutagenic than the emissions from truck oil combustion. The emissions from the vaporizing burner were more mutagenic than the emissions from the atomizing burner, burning either automotive or truck oil. The higher mutagenic activity found in the emissions of the vaporizing burner may be attributed to the higher concentrations of the polycyclic aromatic hydrocarbons emitted by the vaporizing burner as stated previously.

In addition to potential problems posed by increased PAH levels in fuels and emissions, a potential health hazard is also presented by the combination of benzo(a)pyrene and Fe(III) in combustion emissions. As shown in the previous section, the predominant form of iron in waste oil emissions is Fe(III). Lung cancer has been shown to be elevated in hematite miners (22,23). Following this discovery, several researchers found that administration of iron oxide (Fe_2O_3) to the respiratory tract of hamsters by intratracheal instillation, together with benzo(a)pyrene, resulted in an increased yield of tumors, while tumors were not found with ferric oxide alone (24-26). The presence of elevated levels of both Fe(III) oxide and benzo(a)pyrene in these samples indicates that the tumorigenic potential of this matrix should receive further study. While the potential for lead emissions will decrease as lead antiknocking agents are removed from U.S. gasoline supplies, iron (III), an engine wear material, will continue as a major contaminant of used engine oil. If the combination of BaP/Fe(III) is carcinogenic in these emissions, this hazard will persist when crankcase oil is used in space heating applications, especially when used in the air atomization heaters.

In the separate test runs, particulate samples were collected by a massive air volume sampler for several in vitro and in vivo bioassays to evaluate the toxicity of the particles emitted from combustion of the automotive waste crankcase oil using the same two types of burners (27). The particles emitted from both burners produced a dose-related cytotoxic effect in rabbit alveolar macrophages (RAM) in vitro and a dose-related sensory irritant response via intraperitoneal injection in mice. The particles from atomizing burners also resulted in pulmonary injury by intratracheal instillation in hamsters (28). In the host defense infectivity test via intratracheal injection in mice, the particles from the vaporizing burner produced an elevation of mortality whereas the particles from the atomizing burner showed no significant elevation of mortality at the test dose (100 $\mu\text{g}/\text{mouse}$) when compared to the control group of animals. The results of these studies showed that, compared

to the toxicity of other combustion particles, the particles emitted from the combustion of automotive waste crankcase oil in general were comparable in overall potency to the most toxic combustion particles previously tested; i.e., residual oil flyash and some coal flyash samples (29). The high concentrations of heavy metals such as lead and zinc in the particles from waste oil combustion may account for the high toxicity.

IX. Summary and Conclusions

Analysis of elemental species in emission samples from the air atomizing heater confirmed the elevated metal content of waste oil emissions previously identified in the Phase 1 study (1). Bromine levels were exceptionally high, indicating that bromine from gasoline antiknock additives exists as a major constituent of waste crankcase oil and represents a major air emissions constituent from its combustion. The ferrous ion (Fe(II)) content in particulate samples obtained from the air atomizing heater was very low. Based on the assumption that iron exists primarily in ionic forms in combustion emissions, ferric ion (Fe(III)) was determined to be the major Fe species in emissions from the air atomizing heater fired with waste crankcase oil.

Several polycyclic aromatic hydrocarbon (PAH) compounds were found at elevated levels in gaseous emissions from both waste oil space heaters. The vaporizing pot heater emissions had a higher PAH content than did the air atomization heater. Based on the literature, the vaporizing pot burner PAH emissions were also much higher than residential/commercial space heaters fired with conventional fuel oil. For example, benzo(a)pyrene emissions for the vaporizing pot heater were 550 ppb compared to 0.1 ppb for a residential space heater fired with No. 2 oil (4).

In addition to concern about PAH and Fe(III) species in combustion emissions, the elevated level of both of these constituents in combination is cause for even greater concern. Combinations of BaP and Fe(III) have been shown to promote certain types of mammalian cancer.

No organolead compounds were detected in emissions from the air atomization heater. Organolead analyses were not performed on the vaporizing pot burner emissions. Based on this study, waste crankcase oil combustion should be of minor concern for producing organolead emissions in the ambient air.

Mutagenicity assays of the particulate and the XAD samples from both burner types were mutagenic and contained direct-acting mutagens. Emissions from the vaporizing pot burner were more mutagenic than emissions from the air atomizing burner. Comparison of the two types of fuels showed that emissions from the automobile waste crankcase oil were consistently more mutagenic than emissions from the truck waste crankcase oil.

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